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(54) Corrosion inhibition

(57) A method of inhibiting corrosion of iron or steel reinforcement members, present in a concrete structure, comprises incorporating into the concrete slurry from which the concrete structure is to be formed, a corrosion inhibiting amount of a phosphonic acid corrosion inhibitor.

In another embodiment, an existing reinforced concrete structure is repaired by pouring a cement slurry containing a phosphonic acid corrosion inhibitor on top of the structure and allowing the inhibitor to migrate through the structure into contact with the reinforcing members.

Preferred phosphonic acid corrosion inhibitors contain a hydroxy or amino group e.g. 2-hydroxy phosphonoacetic acid.

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FIGURE 1
POLARIZATION RESISTANCE VERSUS TIME
MILD STEEL IN NON-INHIBITED SOLUTION

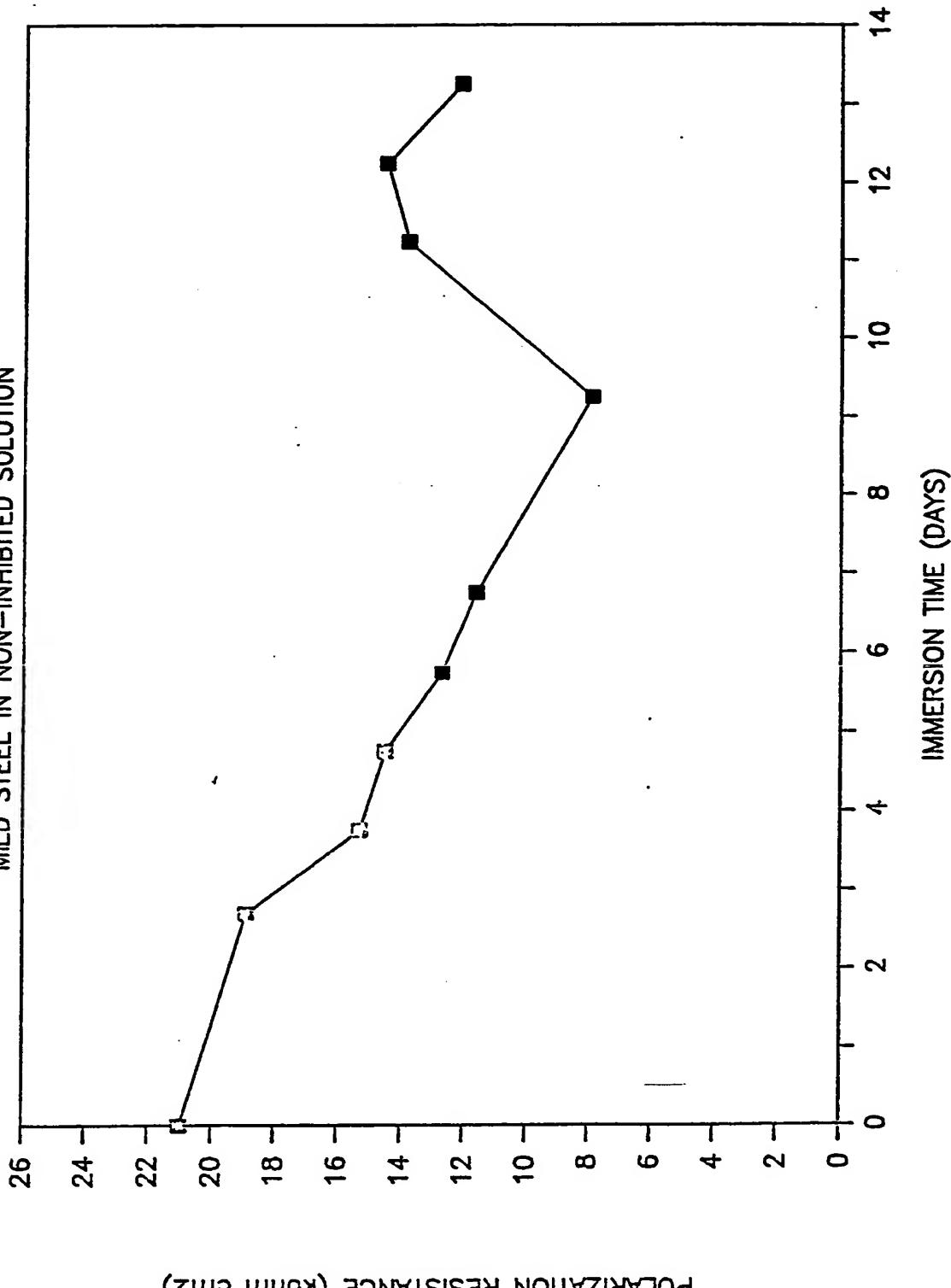
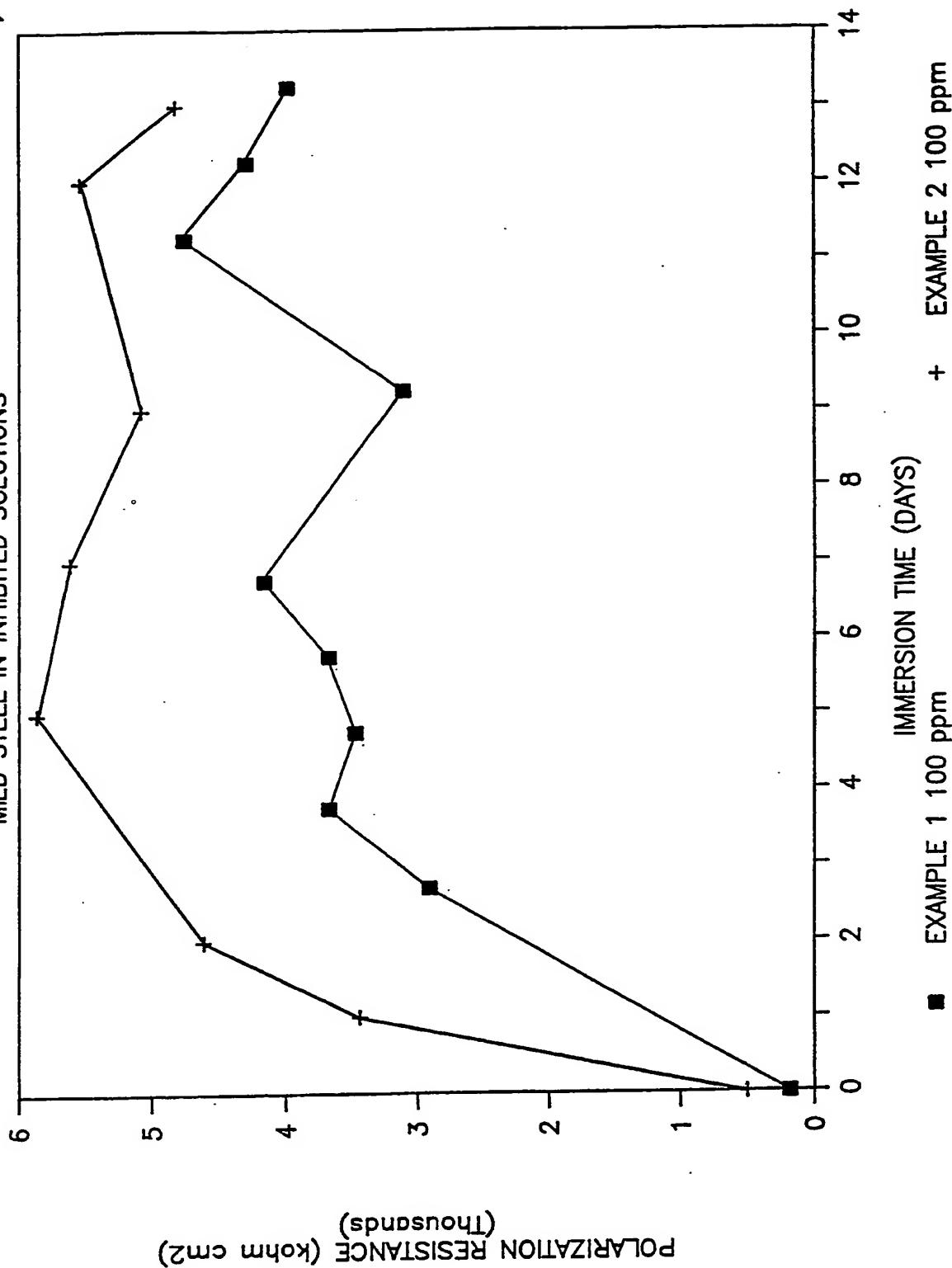


FIGURE 2
POLARIZATION RESISTANCE VERSUS TIME
MILD STEEL IN INHIBITED SOLUTIONS



Corrosion Inhibition

The present invention relates to corrosion inhibition, especially to corrosion inhibition of iron or steel reinforcing bars in concrete structures.

Cement compositions, e.g. Portland cement or sulphate-resisting cements which can be set and hardened by the action of water, are termed "hydraulic cements." In order to improve the strength of concrete structures formed by setting and curing such hydraulic cements, metal bars, often termed "re-bars" are inserted into the cements prior to setting and curing. Like any other metal, such re-bars are susceptible to corrosion, caused by many reasons including e.g. by corrosive setting accelerators, e.g. calcium chloride, contained in the concrete, aggregate or other materials washed by chloride contaminated brackish or sea water, poor quality water used in the concrete mix, poor quality water used in the curing process of the concrete, or from common salt used to de-ice road surfaces. Inhibition of this undesired corrosion has been attempted by cathodic protection of the re-bars or by the application of corrosion inhibition methods to the re-bars.

To date, no entirely satisfactory corrosion inhibitors have been found for this very specific application.

For example, alkali metal nitrites have been used as corrosion inhibitors in cements, as illustrated by U.S. Patent 3210207, U.S. Patent 3801338, U.S. Patent 3976494 and U.S. Patent 4365999. In U.S. Patent 4092109 calcium nitrite is employed as a corrosion inhibitor in steel-reinforced concrete compositions.

There is a need, therefore, for corrosion inhibitors other than nitrites which are expensive and also can cause environmental and/or toxicity problems.

Phosphonates are known to be useful as corrosion inhibitors and/or scale control agents in industrial waters. Industrial water in this instance usually encompasses a pH range of about 6.5 to about 9.5. In most circumstances the chloride content can be expected not to exceed 1000 ppm and is more usually in the range 100 to 500 ppm. Calcium is usually present in such water in an amount of from 100 to 700 ppm represented as ppm calcium carbonate hardness.

In major contrast to this, concrete is a solid which has a porous matrix in which aqueous solutions may be entrained. The pH of this pore solution ranges from 12 to 14, and usually

has saturation levels of calcium ions present. In normal circumstances, mild steel would not corrode (i.e. would be passive) when in contact with aqueous solution having a high pH in the range 12 to 14.

Re-bar corrosion is caused, however, by the presence of several aggressive species in the pore solution. These include sulphate ions, sulphides, and particularly chloride ions, whereby the passivation of the re-bar is disrupted.

We have now found that, surprisingly, phosphonates are effective as corrosion inhibitors in pore solutions having high pH and containing chloride ions, and provide an inexpensive and environmentally acceptable solution to the problem of providing corrosion inhibitors for use in reinforced concrete structures.

Accordingly, the present invention provides a method of inhibiting corrosion of iron or steel reinforcement members present in a concrete structure, comprising incorporating into the concrete slurry from which the structure is to be formed a corrosion - inhibiting amount of a phosphonic acid corrosion inhibitor.

The amount of the phosphonic acid which is incorporated into the concrete slurry in order to be effective as a corrosion inhibitor is normally within the range of from 0.005 to 5% by weight, based on the weight of the concrete slurry.

The phosphonic acid corrosion inhibitor used is preferably one containing a hydroxy or amino group. Examples of amino-phosphonic acids include amino tri(methylenephosphonic acid), ethylenediamine tetra(methylene phosphonic acid), diethylene triaminepenta(methylene phosphonic acid), methylamino di(methylene phosphono) carboxylic acid, 3-hydroxy-3-phosphono butanoic acid and methylamino bis(methylene phosphonic acid) as well as their alkali metal, especially sodium or potassium, or alkaline earth metal, especially calcium and magnesium, salts, or mixed alkali metal-alkaline earth metal salts, or ammonium or substituted amine salts.

More preferred are hydroxy-phosphonic acids such as 1-hydroxy ethylidene-1, 1-diphosphonic acid, tris-hydroxymethyl-ethyl phosphonic acid and, especially 2-hydroxyphosphonoacetic acid, as well as their alkali metal, especially sodium and potassium or alkaline earth metal, especially calcium salts, or mixed alkali metal-alkaline earth metal salts.

Another preferred sub-group of phosphonic acid corrosion inhibitors is that which contains carboxyl groups as well as phosphonic acid groups, e.g. phosphino-carboxylic acids.

If desired, the phosphonic acid corrosion inhibitor may be used in combination with further corrosion inhibitors such as, for example, water soluble zinc salts; phosphates; polyphosphates; 2-phosphonobutane-1,2,4-tri-carboxylic acid, nitrites, for example, sodium nitrites silicates, for example sodium silicate; benzotriazole, 515 methylene bis-benzotriazole or copper deactivating benzotriazole or toluriazole derivatives or their Mannich base derivatives; benzothiazole, for example (2-benzothiazolylthio) succinic acid; mercapto-benzotriazole; N-acylsarcosines; N-acylimino diacetic acids; ethanolamines; fatty amines; and polycarboxylic acids, for example, polymaleic acid and polyacrylic acid, as well as their respective alkali metal salts, copolymers of maleic anhydride, e.g. copolymers of maleic anhydride and sulfonated styrene, copolymers of acrylic acid and hydroxyalkylated acrylic acid, and substituted derivatives of polymaleic and polyacrylic acids and their copolymers.

The present invention also provides a pourable cement slurry, suitable for the manufacture of concrete structures reinforced with iron or steel members, comprising a corrosion inhibitor amount of a phosphonic acid corrosion inhibitor.

Still further, the present invention provides a method for repairing existing concrete structures into which are embedded iron or steel reinforcing members, in which method a cement slurry is poured on top of an already cured concrete structure, comprising incorporating into the concrete slurry a corrosion inhibiting amount of a phosphonic acid corrosion inhibitor; and allowing the phosphonic acid corrosion inhibitor to migrate from the poured-on slurry, through the cured concrete structure, into contact with the reinforcing members.

The following Examples further illustrate the present invention.

Examples 1 and 2

Various materials are evaluated as corrosion inhibitors for re-bars in simulated concrete pore water solutions containing high concentrations of chloride ions.

The evaluation comprises measuring polarization resistance against time of a mild steel electrode (steel specification EN3B, polished to 600 Grit finish on SiC paper), in a simulated pore solution containing chloride. The composition of the pore solution is : 0.1M NaOH, 0.2 M NaCl, 100 ppm Ca²⁺ as Ca Cl₂. The polarization resistance measurements are made using a 3 electrode cell, (saturated calomel reference electrode, platinum foil auxillary electrode and mild steel working electrode) by an EG and G Princeton Applied Research Model 273 potentiostat controlled by an IBM personal computer using EG and G Princeton Applied Research M342 softcorr corrosion software.

To separate samples of this simulated pore solution there are added:

- a) no inhibitor (control);
- b) 100 ppm 2-hydroxy phosphonoacetic acid (Example 1); or
- c) 100 ppm 1-hydroxyethylidene-1,1^l-diphosphonic acid (Example 2).

The results are shown graphically in Fig. 1, relating to the control experiment, and Fig. 2, relating to Examples 1 and 2. The results are summarized in the following Table and show considerably lower corrosion rates are obtained when mild steel specimens are immersed in those high pH, chloride containing solutions with corrosion inhibitor present compared to immersion in solution without corrosion inhibitor (corrosion rates of metals being inversely proportional to their polarization resistance in a given environment).

IMMERSION TIME (DAYS) ON IMMERSION	R _p (kΩcm ²) NO INHIBITOR	R _p (kΩcm ²) EXAMPLE 1	IMMERSION TIME (DAYS) ON IMMERSION	R _p (kΩcm ²) EXAMPLE 2
2.70	21.0	182.0	1	510.2
3.75	18.9	2913	2	3448
4.75	15.3	3677	5	4629
5.75	14.5	3472	7	5880
6.75	12.7	3677	9	5630
9.25	11.6	4167	12	5091
11.25	7.9	3113	13	5555
12.25	13.8	4762		4838
13.25	14.5	4300		
	12.1	3989		

Claims

1. A method of inhibiting corrosion of iron or steel reinforcement members, present in a concrete structure, comprising incorporating into the concrete slurry from which the concrete structure is to be formed, a corrosion inhibiting amount of a phosphonic acid corrosion inhibitor.
2. A method according to claim 1 in which the amount of the phosphonic acid corrosion inhibitor used ranges from 0.005 to 5% by weight, based on the weight of the concrete slurry.
3. A method according to claim 2 in which the amount of the phosphonic acid corrosion inhibitor used ranges from 0.05 to 0.5 by weight, based on the weight of the concrete slurry.
4. A method according to any of the preceding claims in which the phosphonic acid used contains a hydroxy or amino group.
5. A method according to claim 4 in which the amino-phosphonic acid is amino tri(methylene phosphonic acid), ethylenediamine tetra(methylene phosphonic acid), diethylenetriamine penta(methylene phosphonic acid) methylamino dimethylene phosphocarboxylic acid, 3-hydroxy-3-phosphono butanoic acid or methylamino bis(methylene phosphonic acid) or alkali metal salts or alkaline earth metal salts of these compounds.
6. A method according to claim 4 in which the hydroxy-phosphonic acid is 1-hydroxyethylidene-1,1-diphosphonic acid, or 2-hydroxyphosphonoacetic acid, or alkali metal salts or alkaline earth metal salts of these compounds.
7. A method according to any of the preceding claims in which the phosphonic acid corrosion inhibitor is used in conjunction with one or more further corrosion inhibitors.
8. A method according to claim 1 substantially as described with reference to either of the Examples.
9. A pourable cement slurry, suitable for the manufacture of concrete structures reinforced with iron or steel members, comprising a corrosion inhibiting amount of a phosphonic acid corrosion inhibitor.
10. A method for repairing an existing concrete structure, into which iron or steel reinforcing

members are embedded, comprising pouring a cement slurry containing a corrosion inhibiting amount of a phosphonic acid corrosion inhibitor on top of the already cured concrete structure; and allowing the phosphonic acid corrosion inhibitor to migrate from the poured-on slurry, through the cured concrete structure, into contact with the reinforcing members.

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields	Search Examiner
(i) UK CI (Edition K) C1H	MISS M M KELMAN
(ii) Int CI (Edition 5) C23F C04B E04B E04C	
Databases (see over)	Date of Search
(i) UK Patent Office	21 NOVEMBER 1990
(ii) ONLINE DATABASES: WPI CHEM ENG	

Documents considered relevant following a search in respect of claims 1 to 10

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2 194 528 A (SANDOZ) see the examples	9
X	GB 1 556 329 A (BORG-WARNER) see page 3, lines 32 to 34	9
Y	GB 1 556 329 A (BORG-WARNER) see claim 8 and page 2, line 53 to page 3, line 31	1, 10 at least
X	EP 0 343 427 A2 (CASSELLA) see example 17	9
Y	EP 0 322 183 A2 (DOMTAR) see claims 17, 20, 36, 37	1, 9, 10 at least
X	EP 0 166 797 A1 (DOW) see pages 10 and 11	9
X	US 4 786 328 A (AMERICAN STONE-MIX) see the example	9
X	US 4 756 762 A (AMERICAN STONE-MIX) see the example	9
X	SU 1 127 968 A (VOLGA-VRAL) see the examples	9
X	SU 1 076 411 A (CEMENT INDUSTRY RESEARCH INSTITUTE)	9
Y	SU 1 076 411 A	1, 10 at least



Category	Identity of document and relevant passages	Relev& to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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